Art. X.—*On Entropy Meters.*

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(With Diagram).

(1) Introductory.

The physical quantity, termed "the Thermodynamic Function" by Rankine, and the "Entropy" by Clausius—a name which has been finally adopted for it by physicists—is first encountered by the student when he is a little way advanced in the study of the dynamical theory of heat, and he generally finds it a stumbling-block. This is scarcely to be wondered at, seeing that no less a genius than Clerk Maxwell succeeded in giving three different —and totally inconsistent—definitions[1] of this conception in successive editions of his "Theory of Heat." Yet it is definite enough; entropy is as definite a property of any portion of matter as is its volume, or temperature, or pressure. When a body receives heat from external sources its entropy is increased, when it gives up heat its entropy is diminished; the change in the entropy being measured by the ratio which the transferred heat bears to the absolute temperature at which the transfer takes place.

Special interest attaches to entropy, inasmuch as it is the only physical property which always increases when heat is supplied, and diminishes when heat is abstracted. A body may receive heat—*e.g.* during fusion or vaporisation—without rising in temperature ; cases are even known—*e.g.* saturated steam—such that the entrance of heat is accompanied by a fall in temperature. Similarly we do not always find the volume of a body increased by the entrance of heat ; silver iodide contracts when its temperature rises, so does ice during fusion, though both are absorbing heat. But no considerations of this kind come in with regard to entropy ; if heat enter the body its entropy rises,

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[1] Two of these, moreover, were hopelessly wrong ; the third was correct.

if it leave the body its entropy falls; to this rule there are, and can be, no exceptions.

There is no lack, then, of definiteness about this property; the difficulty in grasping its significance is due to its lack of familiarity. We are accustomed to think and speak of volumes and temperatures; probably not one educated man in five could define either accurately, but all are familiar with the terms. The reason for this is, in my opinion, to be found in the fact that instruments for measuring both quantities are in common every-day use; but, so far, we have had no instrument for measuring entropy. The quantity is therefore an unfamiliar one; and the fact that it can easily be calculated from measurements of other quantities helps the student very little in his efforts to gain a clear idea of it.

These considerations—combined with the fact that the instrument, once constructed, would probably be useful—have induced me, for a good many years past, to search for a mode of measuring entropy changes on the scale of a suitable instrument. So far I have not succeeded in constructing a single apparatus which would do this in all possible cases, though I have not yet given up all hope of ultimate success in this direction. The difficulty of the investigation lies in the fact that the change which takes place in the entropy of a body during a transformation is expressed mathematically as the sum of two more or less independent integrals; I do not yet see how an instrument is to be made which will evaluate these simultaneously and add them together.

This difficulty is avoided if we restrict the generality of the apparatus. The restriction is by no means such a disadvantage as it may appear at first sight, seeing that, in the great majority of the transformations we meet with in practice, one or other of the three quantities on which the measurement of the entropy depends is kept constant; only one instrument is then required for observation of the entropy change.

If we design instruments to measure entropy changes at constant pressure, constant volume, and constant temperature, three will be required; one will do the measurements both at constant pressure and constant volume for either solids, liquids, or gases; but two will be required for constant temperature, one

for solids and liquids, the other for gases. Moreover, if the two instruments suited to the particular state of matter under consideration be employed together, the algebraic sum of their indications will give the change of entropy during any transformation, whether the pressure, volume, or temperature be changing, or all three change together; provided that no such change of physical state as fusion or condensation occur during the process.

About two years ago I worked out the first rough ideas of the designs for two entropy meters, working models of which are on the table to-night; but the detailed calculations and the construction of the apparatus were only completed lately.

(2) Entropy Meter for Constant Pressure or Constant Volume.

The construction of this instrument is based on the following considerations :—

If we denote volume by v, absolute temperature by T, pressure by p, quantity of heat by Q, and entropy by ϕ, the definition of entropy gives us at once

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\begin{aligned}
\left(\frac{\delta v}{\delta \phi}\right)_p &= \mathrm{T}\left(\frac{\delta v}{\delta \mathrm{Q}}\right)_p \\
&= \mathrm{T}\left(\frac{\delta v}{\delta \mathrm{T}}\right)_p \div \left(\frac{\delta \mathrm{Q}}{\delta \mathrm{T}}\right)_p \\
&= \frac{\mathrm{T}}{\mathrm{K}_p}\left(\frac{\delta v}{\delta \mathrm{T}}\right)_p
\end{aligned}
$$

where K_p denotes the specific heat at constant pressure

$$
\therefore \left(\frac{\delta \phi}{\delta v}\right)_p = \frac{\mathrm{K}_p}{\mathrm{T}}\left(\frac{\delta \mathrm{T}}{\delta v}\right)_p
$$

$$
\therefore d_p \phi = \frac{\mathrm{K}_p}{\mathrm{T}}\left(\frac{d\mathrm{T}}{\delta v}\right)_p d_p v
$$

$$
= \mathrm{K}_p \cdot \frac{d_p \mathrm{T}}{\mathrm{T}}
$$

Dropping the suffixes and integrating, we have

$$
\int_{\phi_1}^{\phi_2} \delta \phi = \int_{\mathrm{T}_1}^{\mathrm{T}_2} \mathrm{K}_p \cdot \frac{d\mathrm{T}}{\mathrm{T}}
$$

For most bodies K_p is sufficiently nearly a constant between such temperature limits as $0°$ and $100°C.$, and we may replace it in the integral by its mean value ; thus we obtain

$$\int_{\phi_1}^{\phi_2} d\phi = K_p \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\text{or } \phi_2 - \phi_1 = K_p. \log_e \frac{T_2}{T_1}$$

i.e., the change in the entropy during the transformation is proportional to the difference between the napierian logarithms of the final and initial absolute temperatures.

A perfectly similar calculation shews us that the gain of entropy during a transformation in which the body is kept at constant volume is expressed by

$$\phi_2 - \phi_1 = K_v. \log_e \frac{T_2}{T_1}$$

where K_v denotes the specific heat at constant volume. Here again the change in the entropy is proportional to the difference of the logarithms of the absolute temperatures.

We may therefore measure these entropy changes by means of the expansion of mercury. If a mercurial thermometer tube be marked off, not into divisions of equal length, but into lengths proportional to the logarithms of the corresponding temperatures reckoned from absolute zero, its indications will give directly the entropy changes of water, reckoned in thermal units, to about the same order of accuracy as its readings, when it is graduated in the usual way, give absolute temperatures if $273°$ be added to them. For any other substance the readings must be multiplied by the value of the mean specific heat. In this way the first model on the table (Fig. 1) was constructed ; I have merely supplied a thermometer with a scale of napierian logarithms placed opposite to the corresponding temperatures reckoned from absolute zero.

Something more can, however, be done with these instruments than the mere determination of *changes* of entropy. It may frequently be used to measure the entropy of a body from a fixed zero—just as thermometers measure temperatures above and below $0°C.$—provided either its pressure or its volume is supposed to remain constant. The zero of the instrument corresponds to a temperature of $1°$ absolute, or $-272°$ Centigrade, since at this

point the logarithm becomes 0. For temperatures between 1°
and 0° (absolute) the readings will be negative, and pass rapidly
from 0 to $-\infty^y$. It may be objected that entropy is an
essentially positive quantity ; I would answer, so for that
matter is temperature, but no one objects to reckon temperatures
negatively below the melting point of ice.

Entropy Meters for Constant Temperature.

The principle of these is obtained in the following way :—
Employing our old notation, and using in addition the symbol
$\hat{\omega}$ to denote the pressure coefficient, and ϵ to denote the
isothermal elasticity, we may write the second and fourth
thermo-dynamic relations thus :—

$$\left(\frac{\delta\phi}{\delta v}\right)_{\mathrm{T}} = \left(\frac{\delta p}{\delta \mathrm{T}}\right)_v = \hat{\omega}\, p \quad (1)$$

$$-\left(\frac{\delta\phi}{\delta p}\right)_{\mathrm{T}} = \left(\frac{\delta v}{\delta \mathrm{T}}\right)_p = a v \quad (2).$$

Dividing (1) by (2), we obtain

$$-\left(\frac{\delta p}{\delta v}\right)_{\mathrm{T}} = \frac{\hat{\omega}\, p}{a v}$$

$$\text{or} -v\left(\frac{\delta p}{\delta v}\right)_{\mathrm{T}} = \frac{\hat{\omega}\, p}{a}$$

$$\text{but} -v\left(\frac{\delta p}{\delta v}\right)_{\mathrm{T}} = \epsilon$$

$$\therefore a\,\epsilon = \hat{\omega}\, p$$

substitute in (1), we get

$$\left(\frac{\delta\phi}{\delta v}\right)_{\mathrm{T}} = a\,\epsilon$$

$$\therefore d_{\mathrm{T}}\phi = a \cdot \epsilon \cdot d_{\mathrm{T}} v. \quad (3).$$

For all substances a is constant so long as the temperature
does not vary ; ϵ is, under similar circumstances, constant for
solids and liquids, but numerically equal to the pressure for
a gas.

Dropping the suffixes and integrating, we obtain for a solid
or a liquid

$$\phi_2 - \phi_1 = a \cdot \epsilon \cdot (v_2 - v_1)$$

Hence an instrument which measures change of volume can
measure the entropy changes of solids and liquids. I have not

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been able to construct a model for this case, as I do not possess a piezometer.

For a gas, equation (3) becomes

$$d\phi = a \cdot p \, dv.$$

whence (by the gaseous laws) we obtain

$$\phi_2 - \phi_1 = \frac{p_0 v_0}{273} \log_e \frac{p_1}{p_2}$$

Hence entropy change in this case can be measured on a pressure gauge provided with a logarithmic scale, being proportional to the difference of the napierian logarithms of the initial and final pressures.

Here p_0 is one atmosphere, or $1 \cdot 016 \times 10^6$ dynes, and v_0 is the specific volume of the gas under consideration. The latter quantity for air is $773 \cdot 4$ c.m., so $\frac{p_0 \, v_0}{273} = 2 \cdot 88 \times 10^6$

The difference of the napierian logarithms is independent of the value of the unit of pressure. It is convenient, however, to arrange the zero reading to correspond to a pressure of one atmosphere. Hence, if we graduate our scale so that $2 \cdot 88 \times \log_e p$—where p is estimated in atmospheres—corresponds to the division marked 1, the readings will give directly the entropy changes for air, reckoned in millions of mechanical units; to obtain the same quantity for any other gas we have only to divide the readings by the specific gravity of the gas referred to air.

The model shown (see also Fig. 2), is constructed in accordance with these principles; its graduations will measure entropy changes corresponding to an isothermal variation of pressure between $\frac{1}{40}$th of an atmosphere and 2 atmospheres. It is simply an old pressure gauge—recording between these limits—which has been supplied with a new scale. If the results be required in thermal units, all readings must be divided by 42; the quotients give the entropies, measured from the arbitrary zero of the scale, directly in thermal units.

Had the molecular volume been taken for v_0 instead of the specific volume, the instrument would have been direct-reading for all gases.